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Quantum Translator-Rotator: Inelastic Neutron Scattering of Dihydrogen Molecules Trapped inside Anisotropic Fullerene Cages

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We report an inelastic neutron scattering investigation of the quantum dynamics of hydrogen molecules trapped inside anisotropic fullerene cages. Transitions among the manifold of quantized rotational and translational states are directly observed. The spectra recorded as a function of energy and momentum transfer are interpreted in terms of the rotational potential and the cage dimensions. The thermodynamics of orthohydrogen and parahydrogen are investigated through temperature dependence measurements.

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In recent years some remarkable complexes have been synthesized in which a hydrogen molecule is permanently trapped inside a fullerene cage [1–3]. These endohedral H₂-fullerene complexes are superb model systems for understanding quantum molecular dynamics. Because of its low mass and close confinement the H₂ molecule exhibits quantization associated with all of its degrees of freedom. The Pauli exclusion principle also plays an explicit and fundamental role in determining the dynamical behavior, notably through the existence of the nuclear spin isomers, orthohydrogen and parahydrogen.

There has been much interest in the dynamics of H₂ in a variety of porous media, particularly in the context of hydrogen storage [4–6]. The dynamics of several endohedral H₂ fullerenes have been studied by NMR [7,8] and the data have been interpreted alongside models that incorporate quantized rotational and translational states of H₂. However, the energy level separations are very much larger than the characteristic energy scale associated with the magnetic interactions so NMR is only able to probe the translation-rotation manifold indirectly. Infrared spectra [9] have been recorded on endohedral H₂@C60. Here the vibrational states are probed and the translational and rotational splittings may be inferred from the fine structure. However, a fundamental property of quantum translator-rotators is the nuclear spin symmetry and photons are unable to induce the necessary transitions in nuclear spin to probe the translation-rotation manifold directly.

To investigate the quantum motion, inelastic neutron scattering (INS) has a characteristic energy scale that is well matched to the rotational constant and the expected translational splittings. The technique exhibits high sensitivity to incoherent scattering from hydrogen nuclei but importantly the INS interactions are able to induce changes in nuclear spin state; significantly this facilitates transitions between the nuclear spin isomers orthohydrogen and para-

hydrogen. In this first INS investigation of the quantum dynamics of an endohedral H₂-fullerene complex, a cage has been selected that has no symmetry so that the potential energy surface (PES) characterizing the motion is fully anisotropic.

Azacyclic-thiacyclic open-cage fullerene (ATO CF) contains a 13-membered opening through which H₂ has been introduced resulting in the endohedral 1:1 complex, H₂@ATO CF shown in Fig. 1. INS experiments on this complex have been conducted on the IN4 time-of-flight spectrometer at the Institut Laue-Langevin [10]. This instrument has high neutron flux, facilitating measurements on samples that are only available in small quantities. As well as the H₂ inside, the side groups at the cage orifice contain hydrogen nuclei which scatter neutrons. Therefore to measure the spectrum of the entrapped H₂ alone it was expedient to record INS spectra from both H₂-filled and empty cage samples under identical conditions and to determine the difference spectrum. Samples with high purity were prepared using published synthetic procedures

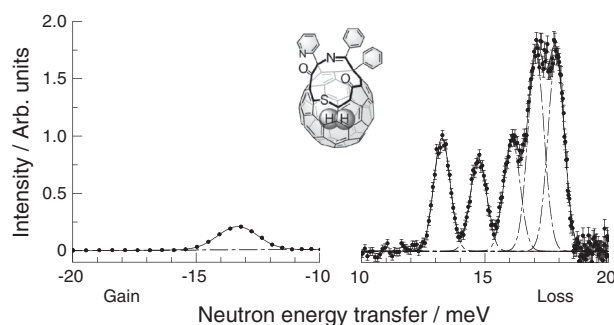


FIG. 1. The INS difference spectrum of hydrogen molecules in H₂@ATO CF recorded at 2.5 K on the IN4 time-of-flight spectrometer; $\lambda_n = 1.8$ Å.

[1,2] The H_2 @ATOCF sample mass was 492 mg, equivalent to 0.46 mmol H_2 .

Figure 1 shows the INS difference spectrum of H_2 molecules trapped in the ATOCF cages. This was recorded at 2.5 K with an incident neutron wavelength $\lambda_n = 1.8 \text{ \AA}$. Time-focusing was optimized for the +15 meV energy transfer region where the instrument resolution is approximately 0.35 meV (half-width at half-maximum: HWHM). However, the resolution varies systematically with energy so, for example, the HWHM is approximately 0.8 meV at -15 meV; all transitions appear with peaks that are resolution limited. A single transition at -13.25 meV appears in neutron energy (NE) gain whereas in NE loss a triplet of lines, +13.25, +14.75, and +16.10 meV, is observed, all with similar amplitude. A more intense band is observed in the region 17–18 meV.

The rotational energy of H_2 is quantized so that $E_J = BJ(J+1)$ where J is the rotational quantum number. Rotational states have degeneracy $2J+1$ with each sub-state labeled by a second quantum number $m_J = J, J-1, \dots, -J$. In free H_2 with a bond length $d_{\text{HH}} = 0.74 \text{ \AA}$, the rotational constant is $B = 7.37 \text{ meV}$ so that the splitting of the $J = 0 \leftrightarrow 1$ rotational transition for free H_2 is 14.74 meV. This coincides with the center line of the observed triplet in NE loss. It is well established that, arising from the exclusion principle, orthohydrogen ($J = 1$) is a nuclear spin triplet with total spin $I = 1$ while parahydrogen ($J = 0$) is a nuclear spin singlet $I = 0$. Therefore orthohydrogen-parahydrogen conversion is spin restricted so, unless time-dependent interactions combining space and spin variables are available, the metastable orthostate becomes trapped when the sample is cooled from high temperature.

The existence of a -13.25 meV NE gain peak at a temperature of 2.5 K proves that the sample is not in full thermal equilibrium. This peak is attributed to trapped ortho- H_2 molecules making transitions to the para- H_2 ground state, while transferring their excess energy to the neutrons.

The NE loss and energy gain spectra are strongly asymmetric at 2.5 K. To investigate further, the temperature dependence of the NE gain region was studied using $\lambda_n = 3.6 \text{ \AA}$ to optimize the energy resolution (0.6 meV HWHM); the spectra are shown in Fig. 2. At 2.5 K the NE gain spectrum comprises simply the -13.25 meV peak but with increase in temperature to 10 K and above, amplitude is systematically transferred to two peaks at higher energy. The peak positions of this triplet coincide with those observed on the NE loss side. Above 80 K the 17–18 meV band also begins to appear in NE gain. The normalized NE gain peak amplitudes are shown in Fig. 3; these were determined by fitting to the spectra in Fig. 2. It is clear that the triplet is associated with the rotational manifold so that in NE gain the neutrons are scattering from orthohydrogen, $J = 1$ to $J = 0$, while in NE loss the

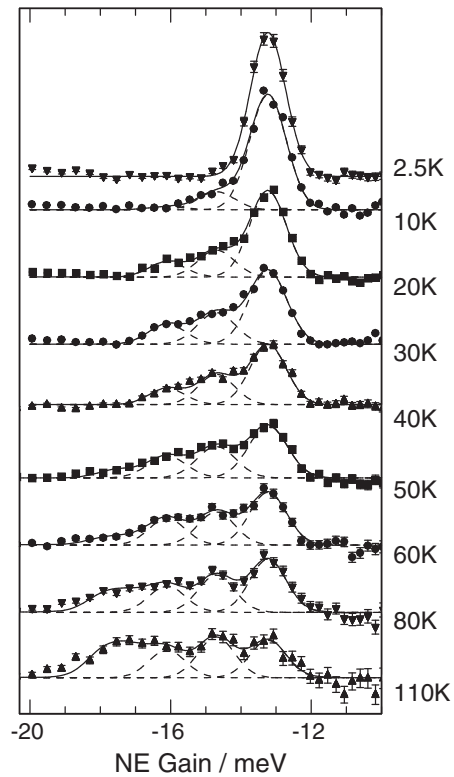


FIG. 2. The temperature dependence of the NE gain spectrum of H_2 @ATOCF; $\lambda_n = 3.6 \text{ \AA}$. The dashed lines are the fitted components of the rotational triplet of orthohydrogen. The solid line includes the translational band at 17–18 meV.

reverse transition from parahydrogen is observed. We assign the triplet to the three states $m_J = 0, \pm 1$ where the degeneracy of the $J = 1$ rotational state has been lifted by the anisotropy of the potential. The solid lines in Fig. 3 are derived from the Boltzmann populations assuming internal

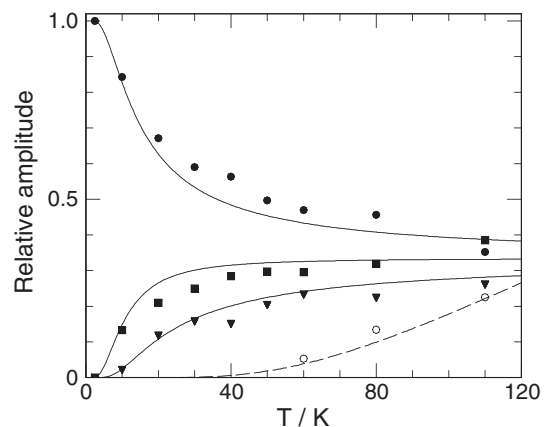


FIG. 3. The temperature dependence of the amplitudes of the rotational triplet observed in NE gain (● 13.25; ■ 14.75; ▼ 16.10 meV). The model assuming thermal equilibration among the rotational triplet is shown with solid lines. Open circles and dashed line; amplitude of the translational doublet.

equilibration amongst the triplet with the observed energy splittings. There is good correspondence with the data so it is evident that the three members of the triplet of orthohydrogen come to internal equilibrium while the species as a whole remains thermally isolated from the lattice.

Additional to changes in neutron energy, the neutron momentum transfer spectrum $S(Q)$ is also available. This can provide information on the physical dimension of the scattering object and on its spatial confinement. The momentum transfer $\hbar Q$ is defined by the wave vectors k of the incident and scattered neutrons, $Q = k_i - k_f$. The double differential neutron scattering cross section for a $J = 1$ to $J = 0$ rotational transition in NE gain converting orthohydrogen into parahydrogen is given by [11,12]

$$\left. \frac{\partial^2 \sigma}{\partial \Omega \partial E} \right|_{1-0} \propto x \frac{k_f}{k_i} S_{1-0}(Q) \delta(E - E_{J'} + E_J), \quad (1)$$

where x is the population of the orthohydrogen species. Applying Refs. [11,12] it may be shown that,

$$S_{1-0}(Q) \propto \exp(-\frac{2}{3}Q^2\langle u^2 \rangle) \sigma_{\text{inc}} [j_1(Qd_{\text{HH}}/2)]^2 \quad (2)$$

where $\frac{1}{3}Q^2\langle u^2 \rangle$ is the Debye-Waller factor, σ_{inc} is the incoherent neutron scattering cross section and $j_n(Qd_{\text{HH}}/2)$ is the n 'th-order spherical Bessel function. In Fig. 4 the Q dependence of the amplitude of the -13.25 meV NE gain peak is shown for $T = 2.5$ K, recorded with $\lambda_n = 1.1$ and 1.24 Å. Equation (2) has been fitted to the experimental data. Apart from an amplitude scaling factor, the only adjustable parameter is $\langle u^2 \rangle$, the mean-square displacement of the hydrogen molecule. The best fit with $\langle u^2 \rangle_{\text{expt}} = 0.068 \pm 0.001$ Å² is shown; solid line, Fig. 4. Very good correspondence with the data is obtained. This provides independent confirmation of the assignment of the triplet to the manifold of rotational lines.

It is clear from Figs. 2 and 3 that the 17–18 meV band belongs to a different manifold. The temperature dependence of the band amplitude is characteristic of a

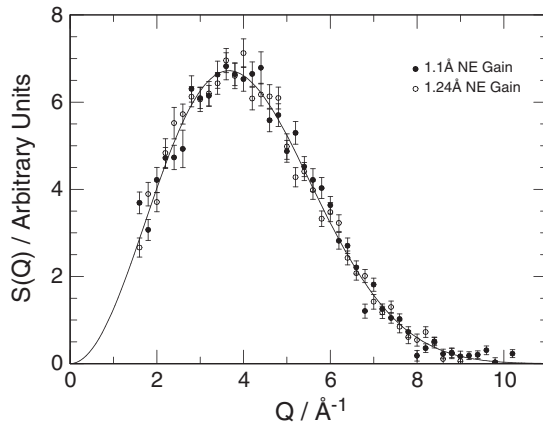


FIG. 4. Neutron momentum transfer spectrum $S(Q)$ for the -13.25 meV rotational line in NE gain: $T = 2.5$ K. The solid line is the fit with Eq. (2).

Boltzmann factor with energy ≈ 17.5 meV; dashed line Fig. 3. The dimension of the fullerene cage has been estimated previously from the molecular structure [7] and to a first approximation the H_2 molecule occupies a sphere with root mean square radius (rms), $r_s = 0.78$ Å. Using this value we are able to estimate the translational splitting. Assuming a spherical cage with infinite walls, the translational eigenfunctions are spherical Bessel functions, $\psi_{\text{trans}}^{(n,l)}$ where n and l are quantum numbers. Applying the normal boundary conditions the eigenfunction solutions can be found numerically. Thus the ground ($n, l = 1, 0$) to first excited ($n, l = 1, 1$) translational splitting is, $\Delta_{\text{trans}}^{1,0-1,1} = 10.32 \frac{\hbar^2}{2\mu r_s^2}$, [7] where μ is the mass of the hydrogen molecule. With $r_s = 0.78$ Å, we calculate $\Delta_{\text{trans}}^{1,0-1,1} = 17.68$ meV in very satisfactory agreement with the center of the observed band.

Additional support for the assignment of this band to H_2 translation is provided by $\langle u^2 \rangle$ determined from the Q dependence of the rotational line. The mean-square displacement of the hydrogen molecule in its ground state may be calculated from the ground state eigenfunction $\psi_{\text{trans}}^{(1,0)}$ leading to $\langle u^2 \rangle_{\text{sph}} = 0.068$ Å². This is in very good agreement with the experimental value determined from Fig. 4. Therefore, although in this provisional analysis the cage has been approximated with spherical shape, a very consistent picture has emerged, confirming the assignments to the rotational and translation manifolds. In fact the translational band has structure and is best fitted as a doublet with energies 17.10 and 17.90 meV. This splitting represents, in part at least, the lifting of the threefold degeneracy.

For free H_2 the $J = 1$ rotational state is threefold degenerate, however, the ATOCF cage is ellipsoidal and so presents an anisotropic PES to the entrapped H_2 . We identify three mutually perpendicular axes XYZ representing the orientation of the H_2 molecule and we shall assume that the potential energy about these axes is dominated by cosine terms with twofold symmetry, reflecting that of the H_2 molecule. If the respective direction cosines of the H-H vector are \cos_X , \cos_Y , and \cos_Z we may write the anisotropic rotational potential as

$$V = V_X(1 - \cos_X^2) + V_Y(1 - \cos_Y^2) + V_Z(1 - \cos_Z^2), \quad (3)$$

where V_X , V_Y , and V_Z represent the amplitudes of the respective barriers to rotation. Numerical solutions of the rotational Hamiltonian $\hat{H}_R = B\hat{J}^2 + V$ have been found in the basis of free-rotor functions; the latter are spherical harmonics. The effect of the anisotropic potential is to lift the rotational degeneracy as observed experimentally. With $V_X = 3.58$, $V_Y = -3.46$, $V_Z = -0.12$ meV the calculated $J = 0 \leftrightarrow 1$ energy transfers are 13.38, 14.86, 16.20 meV, in good agreement with the observed rotational spectrum. There is one axis that is almost neutral to rotation; the remaining two have barrier heights that are less than one-

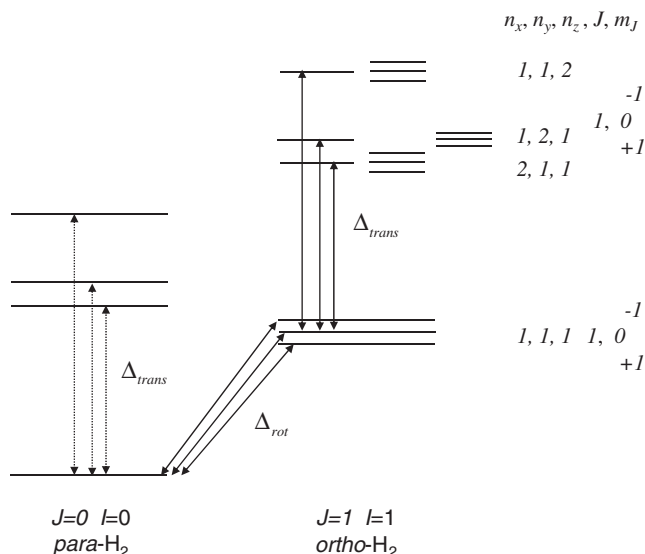


FIG. 5. A schematic showing the low-lying rotational and translational energy levels of H_2 @ATOCF.

half the rotational constant. Therefore, any tunneling effects are minimal and the system is in the free-rotor limit. The eigenfunctions of $J = 1$ are akin to the p orbitals in atomic structure, with $m_J = \pm 1$ mixing equally such that the states with energy 16.26 and 13.38 meV are the real and imaginary combinations. The thermal equilibration among the three rotational substates plays an important role in the NMR spectroscopy and relaxation of the endohedral H_2 fullerenes and the energy levels and splittings determined by INS are in good qualitative agreement with NMR models [7].

An energy level scheme appropriate to H_2 @ATOCF is sketched in Fig. 5. In spherical symmetry the first excited translational state is threefold degenerate but in the presence of an anisotropic cage this degeneracy is fully lifted. In this case the translational states are described by three quantum numbers $n_x, n_y, n_z = 1, 2, \dots$. In INS it may be shown that the translational excitations of orthohydrogen dominate over those of parahydrogen [11]; the scattering is from a compound entity, the H_2 molecule, and pure translational transitions in parahydrogen with $I = 0$ are governed by the coherent scattering cross section, $\sigma_{\text{coh}} = 1.8$ b, which is much smaller than $\sigma_{\text{inc}} = 80.3$ b that governs the translational transitions in orthohydrogen with $I = 1$. This is another manifestation of the nuclear spin symmetry of H_2 so the observed translational peaks arise predominantly from orthohydrogen.

In the spectrum of Fig. 1 two translational transitions are resolved. No rotational fine structure is observed so these features involve no change in m_J . It appears that the third translational transition is absent from the energy window

of Fig. 1. One axis of the ATOCF cage is significantly narrower than the other two with an effective radius estimated to be 0.60 Å compared with a rms radius of 0.78 Å for the cage as a whole [7]. Scaling the observed translations at ≈ 17.5 meV by the factor $0.78^2/0.60^2$ we therefore estimate the energy of the third translational peak to be approximately 29–30 meV. INS spectra have been recorded at these energies: no INS peaks are observed in the range 20–29 meV but a band of overlapping peaks is observed in the range 29–40 meV. However, higher order rotational transitions are also expected in this region along with overtones of the 17–18 meV translational band and cage deformation modes. Subtraction of the empty cage sample is expected to minimize the latter, nevertheless vigilance is required. Further studies are under way to formally identify the third translational mode.

In this first INS investigation of a H_2 molecule inside a fullerene cage the quantization of rotational and translational degrees of freedom has been directly observed. The anisotropy of the PES leads to the degeneracies being fully raised and the rotational potential characterizing the interactions with the cage wall has been determined from the rotational spectrum. The system is a model for quantum dynamics and further investigations are proceeding into the coupling of translational and rotational modes. We are now in the process of combining data from INS, NMR, and infrared spectroscopy to build up a complete picture of the energy level structure for the confined quantum rotor.

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